

Chapter 1

CO₂ Conversion and Utilization: An Overview

Chunshan Song

Clean Fuels and Catalysis Program, The Energy Institute, and Department of Energy
& Geo-Environmental Engineering, The Pennsylvania State University, 209 Academic
Projects Building, University Park, PA 16802

This article provides an introductory overview for defining the scope, potential and limitations of carbon dioxide (CO₂) conversion and utilization. There are various sources of CO₂ emissions, which are dominated by combustion of liquid, solid, and gaseous fuels. The amount of CO₂ consumption for organic chemicals is relatively small compared to CO₂ emitted from fossil fuel combustion. However, CO₂ conversion and utilization should be an integral part of carbon management. Proper use of CO₂ for chemical processing can add value to the CO₂ disposal by making industrially useful carbon-based products. Studies on CO₂ conversion into carbon-based chemicals and materials are important for sustainable development. CO₂ conversion and utilization could also be positioned as a step for CO₂ recycling and resource conservation.

Carbon dioxide, CO₂, is a colorless and odorless gas. The molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O). CO₂ occurs in nature and serves as source of carbon for photosynthesis of plants and crops. It is present in atmosphere with a volumetric concentration of 0.037 % (368 parts per million by volume) as of December 1999 (1). Combustion of most carbon-containing substances produces CO₂. Energy utilization in modern societies today is based on combustion of carbonaceous fuels, which are

VISIT...

LANZAROTE
Caliente.COM

dominated by the three fossil fuels-coal, petroleum, and natural gas. Complete oxidation or combustion of any carbon-based organic matter produces CO_2 , but until recently, CO_2 gas was generally thought to be harmless. In fact, CO_2 plays an important role in the Earth's carbon cycle, and is a necessary ingredient in the life cycle of animals and plants (2, 3). However, CO_2 is also a greenhouse gas (GHG), and the concentration of CO_2 in the atmosphere has increased significantly (1, 4, 5). There are increasing concerns for global warming and thus heightened interest worldwide for reducing the emissions of greenhouse gases, particularly CO_2 (4, 5).

This article is a general overview on CO_2 emissions, CO_2 conversion and utilization. The purposes of this overview are to define the scope, limitations, and potential of CO_2 conversion and utilization, and to discuss the challenges and opportunities, because CO_2 conversion and utilization should be an integral part of carbon management. Specific topical reviews are available on synthesis of organic chemicals by Aresta (6, 7), on chemical conversion of CO_2 over heterogeneous catalysts by Inui et al. (8, 9), Arakawa (10) and Park et al. (11), on synthesis gas production from CO_2 reforming of methane by Rostrup-Nielsen et al. (12, 13), Wang et al. (14) and Bradford and Vannice (15), on reactions in supercritical CO_2 as a reaction medium by Leitner (16) and Subramaniam and Busch (17), on polymer synthesis and processing using supercritical CO_2 by Cooper (18), on thermodynamics of chemical reactions by Xu and Moulijn (19), and on various chemical reactions involving CO_2 in the books by Paul and Pradier (4) and by Halmann and Steinberg (5).

Sources of CO_2 Emissions

The sources of CO_2 emissions include stationary, mobile, and natural sources, as listed in Table 1. The anthropogenic emissions include those from energy utilization in stationary and mobile sources, but exclude natural sources.

Table 2 shows the worldwide CO_2 emissions from the consumption of fossil fuels during 1980-1997 in million metric tons of carbon equivalent (MMTCE) (20, 21). Most countries in the world are consuming fossil fuels in stationary and/or mobile devices and thus contribute to CO_2 emissions.

Table 3 shows the U.S. emissions of CO_2 from different sectors including residential, commercial, industrial and transportation sectors (22, 23). It is clear from Table 3 that every sector is contributing for CO_2 emissions, even the residential homes are responsible because the electricity used in this sector is derived largely by fossil fuel-based electric power plants. During 1980-1997, CO_2 emissions from U.S. industrial sector decreased somewhat (from 484.6 to 482.9 MMTCE), but those from transportation sector increased significantly, from 378.1 to 473.1 MMTCE.

Within the industrial sector, there are two principal routes of CO_2 formation, manufacturing of industrial products where CO_2 is a byproduct from the process (such as the processes for production of cement, limestone, hydrogen, and ethylene oxide), and from energy supply (either as process heat or as electricity) by combustion of fossil fuels which produces CO_2 .

Table 1. Sources of Carbon Dioxide (CO₂) Emissions

Stationary Sources	Mobile Sources	Natural Sources
Fossil Fuel-based Electric Power Plants	Cars, and Sports Utility Vehicles	Humans
Independent Power Producers	Trucks and Buses	Animals
Manufacturing Plants in Industry ^a	Aircrafts	Plant & Animal Decay
Commercial & Residential Buildings	Trains & Ships	Land Emission/Leakage
Flares of Gas at Fields	Construction Vehicles	Volcano
Military & Government Facilities	Military Vehicles & Devices	Earthquake

a) Major concentrated CO₂ sources include plants for manufacturing cement, limestone, hydrogen, ammonia, and soda ash as well as fermentation processes and chemical oxidation processes.

Table 2. World CO₂ Emissions from the Consumption of Fossil Fuels during 1980-1997 (in Million Metric Tons of Carbon Equivalent)

World Regions	1980	1990	1997
North America	1484.2	1561.4	1725.8
Central and South America	173.0	187.4	242.5
Western Europe	1022.1	1011.2	990.2
Eastern Europe & Former U.S.S.R.	1111.4	1297.9	851.8
Middle East	137.2	200.8	264.0
Africa	145.7	198.4	236.4
Far East and Oceania	977.2	1429.9	1921.1
World Total	5050.8	5886.9	6231.7
Selected Countries			
United States	1290.8	1352.1	1488.5
Former U.S.S.R.	807.3	1035.7	N/A
Russia	N/A	N/A	421.8
China	393.0	620.4	821.8
Japan	260.4	273.6	296.7
Germany	N/A	N/A	234.4
Germany, East	82.6	78.4	N/A
Germany, West	207.7	188.8	N/A
United Kingdom	167.7	167.4	156.9
Canada	125.2	127.8	143.4
France	135.4	103.1	101.7
Poland	115.2	90.8	95.2
Italy	102.4	113.3	115.8
Former Czechoslovakia	88.5	79.7	N/A
India	82.2	155.7	237.3
Mexico	68.1	81.2	93.7
South Africa	64.2	80.5	98.9
Spain	59.0	62.0	67.8
Australia	54.3	74.4	88.8
Netherlands	53.3	59.9	64.4
Brazil	51.8	57.7	77.3
Romania	46.8	49.5	31.3
Belgium	37.4	34.2	36.8
Korea, South	35.0	60.6	116.3
Venezuela	25.0	29.8	37.3
Sweden	24.1	14.8	15.1
Indonesia	23.2	40.0	67.1
Turkey	18.0	35.0	44.6
Austria	16.5	16.1	16.8
Switzerland	13.1	12.1	12.6

Sources: DOE, EIA, 1998, 1999; N/A: not available, or not applicable.

Table 4 shows the U.S. CO₂ emissions from electricity-generating units that include both electric utilities and non-utilities (independent power producers) (22, 23). There are far more coal-fired units in the electric utilities, while natural gas-fired units are more popular among the independent producers. Overall, CO₂ emissions from utilities and non-utilities contribute 523.4 and 134.4 MMTCE, respectively. Coal-fired units produced most CO₂ (496.6 MMTCE), followed by gas-fired units (89.3 MMTCE) and petroleum-based units (22.4 MMTCE).

In addition to CO₂, there are several other greenhouse gases (GHGs). Table 5 shows the U.S. emissions of greenhouse gases during 1990-1997, based on a report published in 2000 by the Energy Information Administration of U.S. Department of Energy (24). Methane, nitrous oxides and fluorinated compounds have much stronger greenhouse gas effects than CO₂. However, their amounts are much smaller. The emissions of all the GHGs are shown on the same basis using the same unit of million metric tons of carbon equivalent (MMTCE) based on global warming potential (24). The 1997 GHG emissions in the U.S. reached 1816 MMTCE, including contributions by CO₂ (1505 MMTCE), CH₄ (165 MMTCE), NO_x (103 MMTCE) and other greenhouse gases totaling 38 MMTCE. It is clear from these data that CO₂ is by far the most dominant GHG.

Control of CO₂ Emissions

Figure 1 shows the key issues related to greenhouse gas control and utilization. The basic issues of GHG control involve energy economics, policy regulations, environmental protection and global climate change. Control of CO₂ emissions is among most important areas of GHG control. The anthropogenic emissions of GHGs are due mainly to the fossil energy utilization. The economic development in the U.S. has benefited greatly from relatively cheap energy sources. The idea for regulation of CO₂ emissions by ratifying Kyoto Protocol has not been popular in the U.S., although emissions of pollutants (SO_x, NO_x, CO, HC, particulate matters, etc.) are being regulated strictly in the U.S. On the other hand, carbon tax has already been implemented for CO₂ emissions in some countries in Western Europe.

There are five broadly defined technical options for control of CO₂ emissions: energy choices, energy efficiency, CO₂ capture, CO₂ sequestration, and CO₂ utilization. These options are briefly discussed below.

Energy choice is the basic consideration for selecting the primary energy input for new installations of energy systems or for switching between different forms of energy for existing energy systems. One can reduce the CO₂ emission per million BTU by selecting the less CO₂-intensive form of energy, for example, natural gas versus coal. An empirical rule of thumb is the atomic hydrogen-to-carbon ratio; the higher the H/C ratio, the lower the amount of CO₂ per million BTU. The H/C ratio decreases in the order of natural gas (about 3-4), petroleum (about 1.8-2.0), and coal (about 0.8-1.2). Fuel decarbonization before combustion is an option that is being studied as one way to mitigate CO₂ emissions to atmosphere (5), which is also related to the above discussion with respect to fuel H/C ratio changes.

Table 3. U.S. CO₂ Emissions from Different Sectors (Million Metric Tons of Carbon Equivalent)

CO ₂ Emissions Sources	1980	1990	1997
CO ₂ from Residential Sector	248.4	253.1	286.5
CO ₂ from Commercial Sector	178.3	206.8	237.2
CO ₂ from Industrial Sector	484.6	454.1	482.9
CO ₂ from Transportation Sector	378.1	432.1	473.1
CO ₂ from End-Use Total	1289.4	1346.1	1479.6
CO ₂ from Electric Utilities*	418.4	476.9	523.4

Sources: DOE, EIA, 1998, 1999

*Electric Utility emissions are distributed across end-use sectors.

Table 4. U.S. CO₂ Emission from Electricity-Generating Units (Million Metric Tons of Carbon Equivalent)

CO ₂ Emissions Sources	1990	1995	1997
Coal-Fired Units at Electric Utilities	409.9	434.3	471.3
Petroleum-Fired Units at Electric Utilities	25.3	13.0	15.0
Gas-Fired Units at Electric Utilities	39.2	44.5	36.0
Other Units at Electric Utilities	1.2	0.8	1.0
Emissions at Electric Utilities, Sub-total	475.5	492.7	523.4
Coal-Fired Units at Nonutilities	17.8	24.6	25.3
Petroleum-Fired Units at Nonutilities	4.3	7.3	7.4
Gas-Fired Units at Nonutilities	39.2	57.6	53.2
Other Units at Nonutilities	37.4	45.9	48.4
Emissions at Nonutilities, Sub-total	98.7	135.5	134.4
CO ₂ from Coal-Fired Units, Total	427.7	458.9	496.6
CO ₂ from Petroleum-Fired Units, Total	29.6	20.3	22.4
CO ₂ from Gas-Fired Units, Total	78.4	102.1	89.3
CO ₂ from Other Units, Total	38.5	46.8	49.4
Total CO ₂ Emissions from Generators	574.2	628.1	657.7

Sources: DOE, EIA, 1998, 1999

Table 5. U.S. Emissions of Greenhouse Gases during 1990-1999 Based on Global Warming Potential^a (Million Metric Tons of Carbon Equivalent)

Gas	1990	1995	1997	1999-P
Carbon Dioxide	1,351	1,435	1,505	1,527
Methane	182	179	172	165
Nitrous Oxide	99	106	104	103
HFCs, PFCs, and SF ₆	24	29	35	38
Total	1,655	1,748	1,816	1,833

a) Source: EIA Report, US DOE, EIA/DOE-0573(99), October 31, 2000

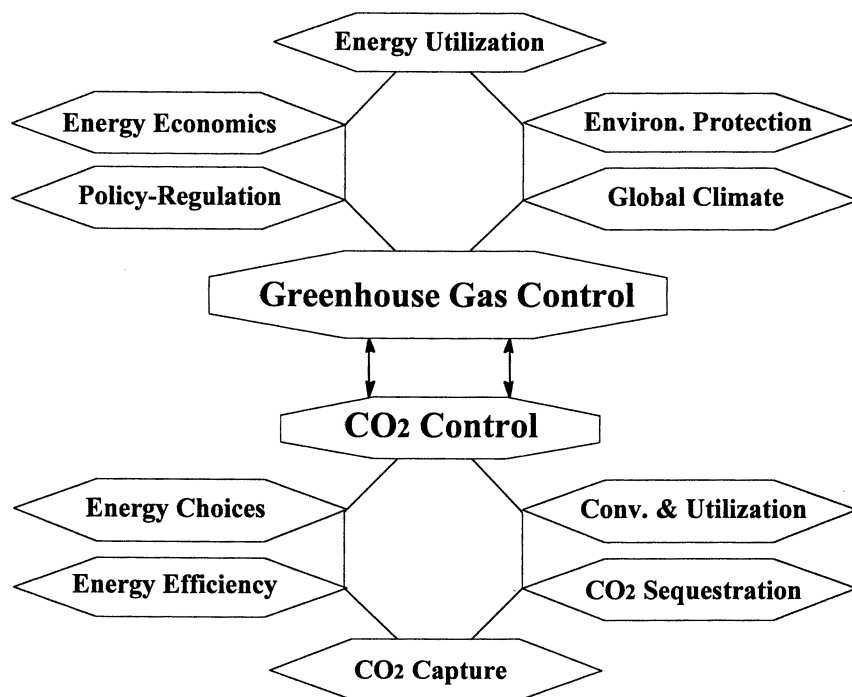


Figure 1. Key issues for control of greenhouse gas and related technical areas for CO₂ control.

An alternative is to use more renewable energy. Common renewable energy forms include hydropower, solar energy, wind energy, and biomass. Biomass and animal wastes are opportunity fuels whose use is also encouraged where available. They are not completely CO₂-neutral, because the collection and transportation of biomass consume energy and fuels. The issues of major concerns on biomass include the regional and seasonal availability as well as energy density and energy demand-supply balance. Combination of biomass with fossil energy in certain ways including conversion is also being explored (25). Solar energy could also be used in selected endothermic chemical processes to reduce the need for using heat from combustion of fossil fuels which also produces CO₂. The issues of concerns for renewable energy in general are energy density, availability, energy efficiency, and capital cost.

Development for improved energy efficiency is an important area that has a major impact on CO₂ reduction. Existing energy utilization systems in the fossil fuel-based electricity generators in the U.S. have an average efficiency of about 35% (26). In other words, about 65% of the useful energy input to the electric power units is wasted as conversion loss. The efficiencies for the automobiles are even lower, less than 20% (27). While significant improvements of energy efficiencies have been achieved in the past decades in power generation technologies and in transportation vehicles, there is a thermodynamic limit for the heat engines by Carnot cycle, which basically dictates the operation. Development and implementation of new energy utilization systems such as IGCC for coal-based power plants, GTCC for natural gas-based power plants, and fuel cell-based hybrid motors for transportation, could increase the energy efficiencies significantly, by 30% or more. The same principle can be applied to chemical industry, where more efficient process or more selective catalyst can make a process such as oxidation reaction more selective such that CO₂ formation is minimized at the source, thus improving the process efficiency, conserving hydrocarbon resource, and reducing CO₂ formation at the source (28).

CO₂ Capture and Sequestration

CO₂ capture involves chemical or physical separation of CO₂ from gas mixtures. Common methods include absorption using an agent such as monoethanol amine, physical adsorption using solid adsorbent, cryogenic separation at low temperatures, and membrane separation (see below). CO₂ sequestration refers to long-term storage of CO₂ in various reservoir locations with large capacity, such as geologic formations, ocean, aquifers, and forest (29-31).

The industrial separation of CO₂ from flue gas of power plants is currently carried out by using absorption process with monoethanol amine as the liquid absorbent (32, 33). It is usually carried out using gas mixtures that contain CO₂ in relatively high concentrations. Large-scale separations in industry are currently based on chemical absorption of CO₂ from concentrated gas mixtures such as flue gases from power plants, from hydrogen plants or

from ammonia plants. The Fluor Daniel ECONAMINE FG CO₂ recovery process that was developed by Dow Chemical is one of the widely used commercial processes (34). The process uses an amine solution, in which a proprietary additive is present, to remove CO₂ economically from low-pressure, oxygen-containing streams such as flue gas. Some recent large-scale designs for CO₂ recovery from flue gas are proposed for use in CO₂-enhanced oil recovery (35). It is known that for the conventional liquid scrubber, the sterically hindered amine requires considerably less energy for regeneration than conventional monoethanolamine (36). A team of researchers at Argonne National Laboratory has conducted a study to identify and evaluate the advantages and deficiencies of several technologies for capturing CO₂ from the flue gas of utility boilers, including chemical solvent, cryogenic, membrane, physical adsorption, and physical adsorption methods (37).

Physical adsorption can be used for separation of gas mixtures. Activated carbons and carbon molecular sieves are readily available commercially, and many studies have been conducted on CO₂ adsorption using such materials. A well-planned and carefully conducted study by Yang and coworkers at SUNY-Buffalo has demonstrated that PSA by using carbon molecular sieve could generate pure CO₂ at low recovery, but generally the kinetic selectivity of CO₂/N₂ is not high enough (38). Separation of CO₂ from air is usually not economical, but there are special applications for such separation in spacecraft using solid sorbent.

CO₂ capture and sequestration (storage) are active areas of study worldwide, and recent reviews are available on the state of the art (29, 31, 33), on the options for CO₂ removal from fossil-fueled power plants (39, 40), on U.S. DOE perspectives (41, 42), on the international perspectives (43), and on the membrane technologies for gas separation in general (44). As indicated in most reviews, technologies for capturing CO₂ are available but are still relatively energy-intensive and thus relatively expensive. Further research, particularly novel approaches, are necessary for lowering the cost of CO₂ utilization. An alternative approach has been proposed to use CO₂ along with H₂O and O₂ in flue gas for tri-reforming of natural gas without CO₂ pre-separation (45).

CO₂ Conversion and Utilization

CO₂ conversion refers to its transformation to chemically different forms that contain the carbon of CO₂ or that makes use of active "oxygen atom" from CO₂. CO₂ utilization includes the uses of CO₂ in both physical processes such as extraction and chemical processes such as chemical synthesis. The objectives of research and development efforts on CO₂ conversion and utilization can include one or more of the following specific goals depending on the applications: (1) to make use of CO₂ for environmentally-benign physical or chemical processing based on the unique physical or chemical properties of CO₂; (2) to produce useful chemicals and materials using CO₂ as a reactant or feedstock; (3) to replace a hazardous substance or a less-effective substance in existing processes with CO₂ as an alternate medium or solvent or co-reactant or

a combination of them; (4) to use CO₂ for recovering energy or for growing biomass while reducing its emissions to the atmosphere by sequestration; (5) to recycle CO₂ as carbon source for chemicals and fuels; (6) to convert CO₂ under geologic-formation conditions into “new fossil” energies.

Table 6 shows the properties of carbon dioxide (2, 3, 46-48). CO₂ may be used as a gas, liquid, and solid. At atmospheric pressure, CO₂ is about 1.5 times as heavy as air (2, 3). CO₂ may be liquefied by compressing to 2 MPa and cooling to -18 °C, or by compressing to higher pressure of 5.78 MPa at 21 °C. If liquid CO₂ is cooled further to -56.6 °C, the pressure drops to 0.518 MPa, solid CO₂ is formed which co-exists with liquid and gaseous CO₂. This is known as the triple point. The solid CO₂ can sublime directly into gas (without going through the liquid phase) upon absorbing heat, and thus it is called dry ice. CO₂ can not exist as liquid below the triple point. If the pressure on dry ice is reduced to atmospheric pressure, the temperature of dry ice drops to -78.5 °C. CO₂ can not be liquefied above 31 °C, the critical temperature. It exists as supercritical fluid when the temperature and pressure are above 31 °C (T_c) and 7.38 MPa (P_c), respectively.

Currently, CO₂ is used as refrigerant for food preservation, beverage carbonation agent, inert medium (such as fire extinguisher), pressurizing agent, supercritical solvent, chemical reactant (urea, etc.), neutralizing agent, and as gas for greenhouses (2, 3, 46, 49). Solid CO₂ (dry ice) has a greater refrigeration effect than water ice. Dry ice is also usually much colder than water ice, and the dry ice sublimates to a gas as it absorbs heat. It should be noted that the use of CO₂ for refrigeration does not contribute to reduction of CO₂ emissions.

Thermodynamics of CO₂ Conversion. Figure 2 illustrates the thermodynamics of CO₂ conversion, where Gibbs free energy of CO₂ and related substances are shown along with CO₂. The data for plotting Figure 2 were taken mainly from two comprehensive chemical handbooks (47, 48). CO₂ is a highly stable molecule. Consequently a substantial input of energy, effective reaction conditions, and often active catalysts, are necessary for chemical conversion of CO₂. In other words, many reactions for CO₂ conversion involve positive change in enthalpy, ΔH, and thus they are endothermic. However, it should be pointed out that the chemical reactions are driven by the difference in Gibbs free energy between the products and reactants at certain conditions, as shown by the equation below.

$$\Delta G = \Delta H - T \Delta S$$

There appears to be some perceptions by many people that CO₂ conversion would be so endothermic that its conversion would not be feasible. It is true that endothermic reactions consume energy. However, endothermic reactions can be feasible and indeed useful. There are many chemical manufacturing plants that are operated based on endothermic reactions in the chemical industry, and these include pyrolysis (thermal cracking) of

Table 6. Physical and Chemical Properties of Carbon Dioxide

Property	Value and Unit
Sublimation point at 1 atm (101.3 kPa)	- 78.5 °C
Triple point at 5.1 atm (518 kPa)	- 56.5 °C
Critical temperature (T_c)	31.04 °C
Critical pressure (P_c)	72.85 atm (7383 kPa)
Critical density (ρ_c)	0.468 g/cm ³ or 468 g/L
Gas density at 0 °C and 1 atm (101.3 kPa)	1.976 g/L
Liquid density at 0 °C and 1 atm (101.3 kPa) 25 °C and 1 atm CO ₂ (101.3 kPa)	928 g/L 0.712 vol/vol
Solid density	1560 g/L
Specific volume at 1 atm and 21 °C	0.546 m ³ /kg
Latent heat of vaporization At the triple point (- 78.5 °C) At 0 °C	353.4 J/g 231.3 J/g
Viscosity at 25 °C and 1 atm CO ₂ (101.3 kPa)	0.015 cP (mPas)
Solubility in water at 0 °C and 1 atm (101.3 kPa) 25 °C and 1 atm (101.3 kPa)	0.3346 g CO ₂ /100 g-H ₂ O or 1.713 mL CO ₂ /mL-H ₂ O at 0 °C 0.1449 g CO ₂ /100 g-H ₂ O or 0.759 mL CO ₂ /mL-H ₂ O at 25 °C
Heat of formation at 25 °C	- 393.5 kJ/mol
Entropy of formation at 25 °C	213.6 J/K•mol
Gibbs free energy of formation at 25 °C	- 394.3 kJ/mol

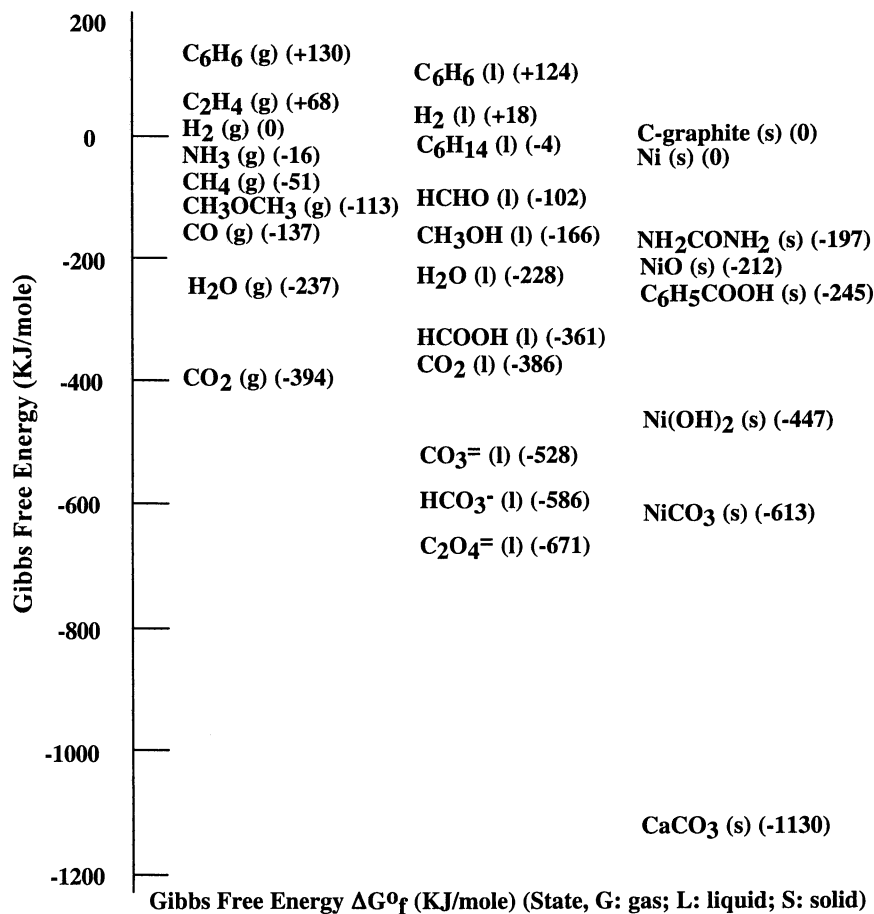


Figure 2. Gibbs free energy of formation for CO₂ and related molecules.

hydrocarbons for manufacture of ethylene and propylene, dehydrogenation reaction for manufacture of petrochemicals such as styrene from ethylbenzene, and steam reforming of hydrocarbons for producing synthesis gas and hydrogen. A simple comparison between steam reforming of methane and CO₂ reforming of methane can illustrate this point. Both reactions are endothermic that require over 200 kJ of energy input per mole of CH₄, but CO₂ reforming requires about 20% more energy input compared to steam reforming. The two reactions give synthesis gas products with different H₂/CO molar ratios; both are useful for certain applications.

A careful analysis of the thermodynamic data in Figure 2 would reveal that it is more energy-demanding if one were to use only CO₂ as a single reactant, but it becomes easier thermodynamically if CO₂ is used as a co-reactant with another substance that has higher Gibbs free energy, such as CH₄, carbon (graphite) and H₂. This trend can also be seen by the change in the reaction heat for reactions with CO₂ as the single reactant [e.g., CO₂ = CO + 1/2 O₂; ΔH° = + 293 kJ/mole CO₂] and with CO₂ as a co-reactant [e.g., CO₂ + H₂ = CO (g) + H₂O (g); ΔH° = + 51 kJ/mole CO₂].

Current Status and Potential Market of CO₂ Utilization. Table 7 shows the 1999 U.S. annual production of CO₂, CO₂-based and CO₂-related chemicals, as well as synthetic organic chemicals and materials (50), in which some 1999 data were derived by estimation based on 1994 data (51). Currently, the U.S. production of liquid and solid CO₂ amounts to 5.36 million tonnes per year (Table 7), which is mainly consumed in the food and beverage industries (refrigerant, coolant, and carbonated drinks). In addition, there are about 10 million tones of CO₂ consumed in making 4.95 million tones of urea fertilizers and 8.47 million tones of urea for chemicals synthesis (Table 7).

The author did an analysis by calculation to set the potential upper limit of hypothetical CO₂ demand for making organic chemicals and materials. Table 7 also shows the potential upper limit of CO₂ demand estimated by the author for chemicals and materials. The methodology of estimation used here is based on that used by Steinberg (5) with modification by considering carbon equivalence in this work. Steinberg used the production data for the plastics in the U.S. in 1980 (5). The present estimation for the carbon-based synthetic materials is based on the U.S. production of plastics, fibers, and rubbers in the 1999 (50). If we assume that the potential upper limit of chemical market demand is that for making all the carbon-based synthetic materials plus several CO₂-related major chemicals and materials using CO₂, then the upper limit of potential CO₂ demand for synthetic organic chemicals and polymer materials could increase to 44.41 million metric tons of carbon equivalent (Table 7). This calculated numbers all correspond to a stoichiometric reaction system where all the carbon in CO₂ is converted to the chemicals (urea, methanol, etc.) and synthetic polymer materials (plastics, fibers, rubbers). This is, of course, a hypothetical scenario, but it does provide an useful measure in terms of order of magnitude.

Table 7. U.S. Production of Synthetic Plastics and Related Chemicals in 1999 and Estimated Potential Upper Limit of CO₂ Demand for Chemicals and Materials

Chemicals & Materials	Production in Common Units ^a	Metric Tons (Tonnes)
Synthetic Plastics:	80,727 millions of lb	36,650,058
Synthetic Fibers	10,219 millions lb	4,639,426
Synthetic Rubbers	2,414 thousands of metric tons	2,414,000
	1. Polymers Subtotal (1999) =	37,584,996 as C 43,703,484 as Comp
Ammonia (reference for urea) (1999) ^a	14,972 thousands of tons	13,579,604
Urea for fertilizer (1999) ^{a,b}	5,453 thousands of tons	4,945,871
Urea for chemicals (1999) ^{a,b}	18,660 millions of lb ^b	8,471,640
Urea for chemicals (1994) ^c	15.90 billions of lb (7,952 thousands of tons)	7,218,600
	2. Urea-equivalent CO ₂ (1999)=	2,686,185 as C 9,839,508 as CO ₂
Methanol for chemicals (1994) ^c	12.18 billions of lb	5,529,720
	3. MeOH-Equivalent CO ₂ (1999) ^f	2,428,590 as C 8,895,937 as CO ₂
CO ₂ - Liquid+Solid (1994) ^{c,d}	11.80 billions of lb (5,899 thousands of tons)	5,357,200
	4. Liquid+Solid CO ₂ (1999) ^e	1,711,143 as C 6,267,924 as CO ₂
Ultimate U.S. CO ₂ demand for chemicals & materials	Total US Potential (1+2+3+4) =	44.4 MMT ^g as C 162.8 MMT as CO ₂
Ultimate world CO ₂ demand for chemicals & materials	Estimated for World Potential	177.6 MMT as C 651.3 MMT as CO ₂

a) Source: ACS. Facts & Figures for the Chemical Industry. C&EN, June 26, 2000, 48-89; b) A significant fraction of the urea is used for making thermosetting plastics that are included in synthetic plastics (2,691 millions of lb urea-based thermosetting resins were produced in 1999); c) Source: ACS. Facts & Figures for the Chemical Industry. C&EN, June 24, 1996, 38-79; d) Liquid and solid CO₂ only; e) 1999 production of liquid+CO₂ was estimated (as 1.17 times 1994 production); f) 1999 production of methanol was estimated (as 1.17 times 1994 production); g) MMT: Million metric ton.

The upper limit of potential market demand worldwide for CO₂ in making organic chemicals and materials is estimated to be 178 million metric tons of carbon equivalent. The detailed statistical data of chemicals production in 1999 are not available for all the countries in the world, but the author did a simplified estimation based on the U.S. chemical production. U.S. chemical industry is the largest in the world, and the plants in the U.S. provide 24% of the world's total chemical production (52). Consequently, the upper limit of potential market demand for CO₂ in the world is estimated by the author to be 4 times that for the U.S.

Table 8 shows the U.S. production of liquid fuels in 1999 (26). The amount of liquid fuels consumed in the U.S. has reached 13.60 million barrel per day, in which 12.75 million barrels per day liquid fuels were used for transportation fuels. By simple calculation of carbon equivalence, it becomes apparent that the liquid fuels correspond to a very large amount of carbon that is on the same order of magnitude with the CO₂ emitted from fossil fuel-based electric power plants in the U.S., as can be seen from Table 8. The total production of liquid fuels in the world is estimated to be about 4 times of the U.S. annual production, based on the fact that U.S. petroleum consumption is about 25% of the world total consumption (26).

Table 9 shows the order of magnitude estimates by the author for CO₂ utilization, based on the data shown in Tables 7 and 8. For comparison, Table 10 shows the order of magnitude estimates published in a recent review by Herzog for the worldwide capacity of various options for CO₂ sequestration (31). The worldwide capacity for utilization of CO₂ for making chemicals and materials is less than 1 Giga tonnes of carbon per year, which is relatively small compared to the several other options such as ocean sequestration. However, it should be noted that the amount of CO₂ that can be utilized for making chemicals and materials can be potentially large enough for expanding commercial-scale applications worldwide.

Challenges and Strategies for CO₂ Conversion and Utilization

Figure 3 is an outline of possible chemical processes that may be used for CO₂ conversion and utilization. There are non-catalytic chemical processes, processes using heterogeneous or homogeneous catalysis, photo-chemical and photo-catalytic reduction, bio-chemical and enzymatic conversion, electro-chemical and electro-catalytic conversion, as well as solar-thermal/catalytic processes. Most of the processes are subjects of research in the laboratory, and few processes have reached large-scale production. A number of reviews have been published concerning various chemical reactions and processes for chemical conversion of CO₂ (4-19, 43, 53, 54).

There exist some chemical processes for CO₂ conversion in chemical industry, for which synthesis of urea from ammonia and CO₂ [$\text{CO}_2 + 2 \text{NH}_3 = \text{H}_2\text{N-CO-NH}_2 + \text{H}_2\text{O}$] and the production of salicylic acid from phenol and CO₂ [$\text{C}_6\text{H}_5\text{-OH} + \text{CO}_2 = \text{C}_6\text{H}_5(\text{OH})\text{COOH}$] are representative examples. Urea is used for making various polymer materials and also for producing fertilizers. As

Table 8. U.S. Production of Liquid Fuels in 1999

U.S. Fuels	1999 Daily Production ^a	1999 Annual Production	Total Annual Production ^b	C-Equivalent of Annual Prod ^c
	Million barrels per day	Million barrels per Year	Million Metric Tons (Tonnes)	Million Metric Tons (Tonnes)
Gasoline	8.38	3058.7	354.8	301.6
Distillate Fuels (Diesel, etc)	3.55	1295.8	171.0	145.4
Jet Fuel	1.67	609.6	77.4	65.8
	Total = 13.60 [12.75 in transportation]		U.S. total =	512.8
			World liquid fuel ^d =	2051.2
			1997 US Electric Utilities Annual CO ₂ Emissions	523.4 as C

a) Source: EIA, AER, US DOE, 2000.

b) 1 barrel of oil (US) = 42 US gallons = 0.15899 cubic meters (m³) = 158.99 liters. Assume average density values of the fuels at ambient temperatures as follows: 0.73 g/mL for gasoline; 0.80 g/mL for jet fuel; 0.83 g/mL for distillate fuels (diesel fuel and heating oils).

c) Assume the average carbon content in the liquid fuels is 85 wt%.

d) Estimated based on the fact that U.S. petroleum consumption is about 25% of the world's total consumption.

Table 9. Order of Magnitude Estimates for the Worldwide Capacity of CO₂ Utilization

Option of CO ₂ Utilization	Worldwide Capacity
	(Order of Magnitude in Giga Ton Carbon)
Non-chemical Utilization	0.01 – 0.1 GtC per year
Chemicals & Materials ^a	0.1 – 1 GtC per year
Synthetic Liquid Fuels ^a	1 – 10 GtC per year

a) Estimated by C. Song based on the U.S. and the world production of chemicals and materials as well as liquid fuels in 1999.

Table 10. Order of Magnitude Estimates for the Worldwide Capacity of Various Sinks^a

Sequestration Option	Worldwide Capacity
	(Order of Magnitude in Giga Ton Carbon)
Ocean	1000s GtC
Deep saline Formations	100s – 1000s GtC
Depleted Oil and Gas Reservoirs	100s GtC
Coal Seams	10s – 100s GtC
Terrestrial	10s GtC
Utilization (Chemical Conversion)	< 1 GtC per year

a) Source. H. J. Herzog. Using Carbon Capture and Sequestration technologies to Address Climate Change Concerns. Am. Chem. Soc. Div. Fuel Chem. Prepr., 2001, 46(1), 53-55.

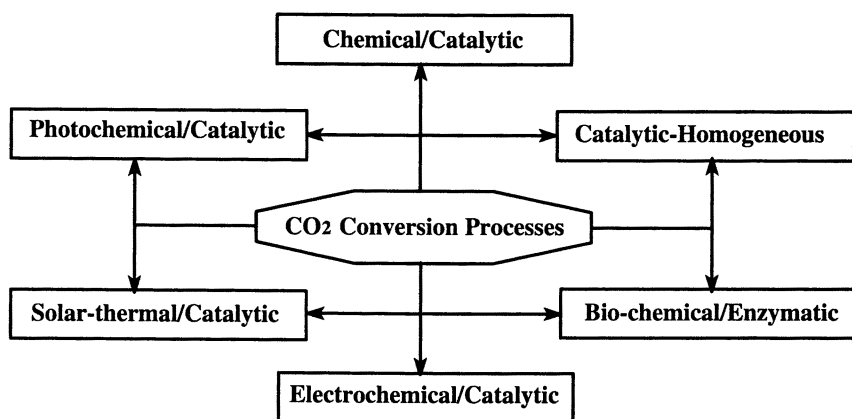
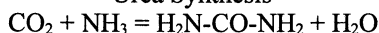


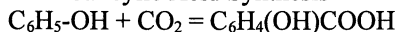
Figure 3. Chemical processes for CO₂ conversion and utilization.

an example of the usefulness of salicylic acid, acetyl salicylic acid is used for making Aspirin, a common medicine.

Urea Synthesis



Salicylic Acid Synthesis



Barriers for CO₂ Conversion and Utilization. There are significant barriers for promoting or enhancing utilization of CO₂ in chemical processes. Such barriers and possible strategies to overcome them are briefly outlined below.

- **1) Costs of CO₂ capture, separation, purification, and transportation to user site.**

One of the strategies would be to identify and use concentrated CO₂-containing gas mixtures at or near the sites of chemical conversion and utilization. From the separation side, better separation methods and improved engineering of separation process can lower this barrier.

However, if it is beneficial and practically applicable, a new processing scheme for using CO₂ in gas mixture without pre-separation of CO₂ would be desired. A proposed new approach is to make industrially useful synthesis gas with desired H₂/CO ratios by using CO₂ along with H₂O and O₂ in flue gas for tri-reforming of natural gas without CO₂ pre-separation (45).

- **2) Energy requirements of CO₂ chemical conversion (plus source & cost of H₂ if involved).**

The corresponding strategies are to use CO₂ as a co-reactant along with one or more compounds that have higher Gibbs free energies, and to identify and use an effective catalyst that can give higher conversion at lower temperatures. CO₂ reduction by hydrogenation has been studied and reported by many research groups. For such processes, H₂ will need to be made from processes that do not co-produce CO₂. It should be noted that H₂ is currently produced by reforming of hydrocarbons which is an energy-intensive process and accompanied by CO₂ formation both from the conversion process and from the combustion of the fuels which is used to provide the process heat (54).

- **3) Market size limitations, and lack of investment-incentives for CO₂-based chemicals.**

The estimated or perceived market sizes for CO₂ conversion vary for different applications. If all carbon-based synthetic chemicals and materials can be made using CO₂, then the current annual production of such chemicals and materials could provide an estimated upper limit of market demands for CO₂ for chemicals and materials.

- **4) Lack of socio-economical and political driving forces that facilitate enhanced CO₂ utilization.**

There are several ways for an industrialized society to encourage more utilization of CO₂. If an environment-conscious society wants to promote CO₂ utilization, various incentives could be given to manufacturers that produce useful chemicals and materials using CO₂, or make use of CO₂ for environmentally-benign processing (such as replacement of phosgene). If the consumers and buyers in the industrialized societies recognize the need to such a level as to support CO₂ utilization, price differential could be instituted for CO₂ utilization which may be characterized as “carbon pricing for greenness”.

Strategy for Research on CO₂ Utilization. The strategic directions for research and development on CO₂ utilization may include but are not limited to the following considerations along with some specific examples. Figure 4 illustrates the utilization of CO₂ with and without chemical conversion processing.

- **1) To produce useful chemicals and materials using CO₂ as a co-reactant or co-feed.**

Many processes could be designed for using CO₂, but the chemicals and materials that have large market demands are relatively limited. An existing industrial process is urea synthesis, which has already found industrial application as fertilizer and as monomer for thermosetting polymers. Expanding applications of urea-based polymers can create more demand on CO₂ and NH₃ for urea synthesis. For the development of new processes, one of preferred approaches is to explore alternate processes for using CO₂ as a co-reactant in making chemicals that have relatively large market or potentially large demand in the near future.

Production of synthesis gas would fit in this category. Synthesis gas with desired H₂/CO ratios can be used for synthesizing chemicals such as methanol and acetic acid by oxo synthesis, olefinic chemicals and ultra-clean hydrocarbon fuels by Fischer-Tropsch synthesis, and also for electricity generation by using either the GTCC (gas turbine combined cycle) or high-temperature fuel cells such as molten carbonate fuel cells or solid-oxide fuel cells. Using CO₂ and methane by dry reforming alone or in combination with steam reforming, and the synthesis of methanol and synthesis of hydrocarbon chemicals using CO₂-rich synthesis gas would fit in this category. Because of the problem of carbon formation and the limited applications of the synthesis gas with low H₂/CO ratios (around 1) from CO₂ reforming, the combined reforming that involves both CO₂ reforming and steam reforming may be preferred for large-scale applications (13, 45, 55).

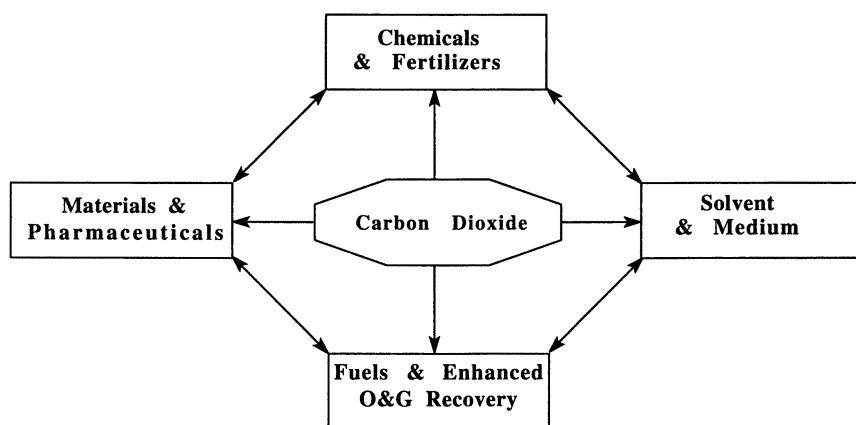


Figure 4. Utilization of CO₂ with and without chemical conversion processing.

- **2) To make use of CO₂ based on the unique physical or chemical properties of CO₂ such as supercritical extraction using SC-CO₂ as a solvent.**

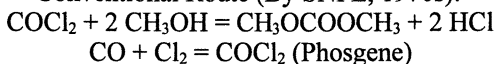
Environment-friendly and energy-efficient processes can be designed by using CO₂ for separation and chemical reaction and materials synthesis. For example, supercritical CO₂ can be used as either a solvent for separation or as a medium for chemical reaction, or as both a solvent and a reactant. Use of supercritical CO₂ (SC-CO₂) allows contaminant-free supercritical extraction of various substances ranging from beverage materials (such as coffee bean), foods (such as potato chips), and organic and inorganic functional materials, to herbs and pharmaceuticals and soils.

Some chemical reactions can benefit from using CO₂ as a mild oxidant, or as a selective source of “oxygen” atoms. For example, the use of CO₂ has been found to be beneficial for selective dehydrogenation of ethylbenzene to form styrene, and for dehydrogenation of lower alkanes such as ethane, propane and butane to form ethylene, propylene, and butene, respectively. Some recent studies have been reviewed by Park et al. on heterogeneous catalytic conversion using CO₂ as an oxidant (11).

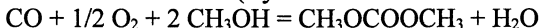
- **3) To replace a hazardous or less-effective substance in existing processes with CO₂ as an alternate medium or solvent or co-reactant or a combination of them.**

Some of the existing industrial chemical processes use hazardous substances as reactant or reaction medium which could be replaced by CO₂ or supercritical CO₂. One area in this category is replacement of phosgene by CO₂, which has been discussed by Aresta for various chemical processes (56). Shown below is a comparison of different chemical processes for making dimethyl carbonate, an industrially useful chemical. U.S. phosgene use was estimated to be about 1.2 million tonnes per year (56, 57). In terms of environmental benefits, the new CO₂-based route is superior to the existing industrial processes that are based on either phosgene or CO, as both chemicals are toxic.

Conventional Route (By SNPE, 1970s):



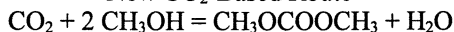
EniChem DMC Process (By EniChem – 12000 tons/Yr)



Ube DMC Process (By Ube Chemical – 3000 tons/Yr)



New CO₂-Based Route



More recent studies by Dibenedetto and Aresta (58) have shown that direct oxidative carboxylation can be achieved using an olefin and CO_2 under an oxidative condition, which can produce the cyclic carbonate chemicals that are currently synthesized in industry by using phosgene.

- **4) To use CO_2 for energy recovery while reducing its emissions to the atmosphere by sequestration.**

CO_2 in flue gas from power plants may be used for enhanced recovery of oil and natural gas, and for enhanced coal bed methane recovery. For enhanced oil recovery, the requirement for CO_2 purity is minimum, and thus the cost of gas processing (prior to use) is lower.

Another approach in this direction is the so-called ocean fertilization which make use of CO_2 in specific locations in the ocean and sun light to grow biomass (59).

- **5) To recycle CO_2 as C-source for chemicals and fuels.**

Recycling of CO_2 as carbon source for chemicals and fuels should be considered for applications where CO_2 can be used that have desired environmental benefits. Although permanent storage seems preferred for carbon sequestration, CO_2 recycling would also make sense if such an option can indeed lead to less consumption of carbon-based fossil resources without producing more CO_2 from the whole integrated system.

The amount of liquid fuel consumed in the U.S. has reached 13.60 million barrel per day, which correspond to a very large amount of carbon that is estimated to be on the same order of magnitude with the CO_2 emitted from fossil fuel-based electric power plants. The proposed approaches include hydrogenation of CO_2 with H_2 to methanol (60, 61), and conversion of CO_2 in flue gas by tri-reforming to synthesis gas ($\text{CO} + \text{H}_2$) with desired H_2/CO ratios for chemicals and fuels synthesis (45).

- **6) To convert CO_2 under geologic-formation conditions into “new fossil” energies.**

Existing fossil fuels are believed to have originated from bio-chemical and geo-chemical transformations of organic substances that were initially present on the surface of the earth over the course of millions of years, which may be viewed as a detour in the carbon cycle. For example, numerous studies have shown that coal was formed from bio-chemical degradation and geo-chemical maturation of higher plant materials that were formed initially on the surface of the earth via photosynthesis from CO_2 and H_2O . A new way of thinking has led to approaches of converting CO_2 directly in geologic formations during its long-term storage. This is still a new topic for which only a few reports are available (62-64).

Conclusions

CO₂ conversion and utilization is an important part of CO₂ management strategy, although the amount of CO₂ that can be converted to chemicals and materials is relatively small compared to the amount of anthropogenic CO₂ emitted from fossil fuel combustion. CO₂ is a carbon source and a unique substance, and CO₂ utilization represents an important aspect of greenhouse gas control and sustainable development.

Proper and enhanced uses of CO₂ can have not only environmental benefits, but also add value to the CO₂ disposal by making industrially useful carbon-based chemical products. There exist barriers and challenges for promoting CO₂ utilization, which include but are not limited to the following: 1) Costs of CO₂ capture, separation, purification, and transportation to user site; 2) Energy requirements of CO₂ chemical conversion (plus source & cost of H₂ if involved); 3) Market size limitations, and lack of investment-incentives for CO₂-based chemicals; and 4) Lack of socio-economical and political driving forces that facilitate enhanced CO₂ utilization.

The following strategic considerations may be helpful for future directions: 1) To produce useful chemicals and materials using CO₂ as a co-reactant or co-feed; 2) To make use of CO₂ based on the unique physical or chemical properties of CO₂ such as supercritical extraction using SC-CO₂ as a solvent; 3) To replace a hazardous or less-effective substance in existing processes with CO₂ as an alternate medium or solvent or co-reactant or a combination of them; 4) To use CO₂ for energy recovery while reducing its emissions to the atmosphere by sequestration (storage); 5) To recycle CO₂ as C-source for chemicals and fuels; and 6) To convert CO₂ under geologic-formation conditions into “new fossil” energies.

Acknowledgments

The author gratefully acknowledge the helpful discussions with Prof. Michele Aresta of University of Bari, Italy, Prof. Tomoyuki Inui of Air Water Inc. (formerly at Kyoto University), Japan, Dr. John Armor of Air Products and Chemicals Inc., Mr. Howard Herzog of Massachusetts Institute of Technology, Dr. David Beecy, Dr. Robert Kane, Dr. Curt White, Dr. Robert Warzinski and Dr. Donald Kraftsman of U.S. Department of Energy, Dr. Meyer Steinberg of Brookhaven National Laboratory, Prof. Alan Scaroni and Prof. Harold Schobert of Pennsylvania State University, Mr. Wei Pan and Dr. Srinivas Srimat of Pennsylvania State University. The research on tri-reforming by the author received financial support by UCR Innovative Concepts Program of U.S. Department of Energy (DE-FG26-00NT40829).

References

1. Keeling, C. D.; Whorf, T. P. Atmospheric CO₂ Records from Sites in the SIO Air Sampling Network. In *Trends: A Compendium of Data on Global Change*. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U. S. Department of Energy, Oak Ridge, TN, U.S.A., August 2000.
2. Lindsey, J. S. Carbon Dioxide. McGraw-Hill Encyclopedia of Chemistry, McGraw-Hill, Second Edition, New York, 1993, pp. 157-159.
3. Pierantozzi, R. Carbon Dioxide. Kirk-Othmer Encyclopedia of Chemical Technology. Fourth Edition. Vol. 5, John Wiley and Sons, New York, 1993, pp. 35-53.
4. Paul, J.; Pradier, C.-M. (Eds.). Carbon Dioxide Chemistry: Environmental Issues. Royal Society of Chemistry, Cambridge, UK, 1994, 405 pp.
5. Halmann, M. M.; Steinberg, M. Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology. Lewis Publishers, Boca Raton, FL, 1999, 568 pp.
6. Aresta M. Perspectives of Carbon Dioxide Utilisation in the Synthesis of Chemicals. Coupling Chemistry with Biotechnology. Stud. Surf. Sci. Catal., 1998, 114, 65-76.
7. Aresta, M. Key Issues in Carbon Dioxide Utilisation as a Building Block for Molecular Organic Compounds in the Chemical Industry. In *CO₂ Conversion and Utilization*. Song, C.; Eds.; Gaffney, A. M.; Fujimoto, K. American Chemical Society, Washington DC, 2001, in press.
8. Inui, T.; Anpo, M.; Izui, K.; Yanagida, S.; Yamaguchi, T. (Eds.). Advances in Chemical Conversions for Mitigating Carbon Dioxide (Studies in Surface Science and Catalysis, Vol. 114), Elsevier, Amsterdam, 1998, 691 pp.
9. Inui, T. Effective Conversion of CO₂ to Valuable Compounds by Using Multi-functional Catalysts. In *CO₂ Conversion and Utilization*. Song, C.; Gaffney, A. M.; Fujimoto, K.; Eds.; American Chemical Society, Washington DC, 2001, in press.
10. Arakawa H. Research and Development on New Synthetic Routes for Basic Chemicals by Catalytic Hydrogenation of CO₂. Stud. Surf. Sci. Catal., 1998, 114, 19-30.
11. Park, S.-E.; Yoo, J. S.; Chang, J.-S.; Lee, K.Y.; Park, M. S. Heterogeneous Catalytic Activation of Carbon Dioxide as an Oxidant. Am. Chem. Soc. Div. Fuel Chem. Prepr., 2001, 46(1), 115-118.
12. Rostrup-Nielsen, J.R. Aspects of CO₂-Reforming Of Methane. Stud. Surf. Sci. Catal., 1994, 81, 25-41.

13. Rostrup-Nielsen, J.R.; Hansen, B. J.H.; Aparicio, L.M. Reforming of Hydrocarbons into Synthesis Gas on Supported Metal Catalysts. *Sekiyu Gakkaishi*, 1997, 40 (5), 366-377.
14. Wang, S.B.; Lu G.Q.M.; Millar, G.J. Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art. *Energy & Fuels*, 1996, 10 (4), 896-904.
15. Bradford, M.C.J.; Vannice, M. A. CO₂ reforming of CH₄. *Catal. Rev.-Sci. Eng.*, 1999, 41 (1), 1-42.
16. Leitner, W. Reactions in Supercritical Carbon Dioxide (scCO₂). *Top. Curr. Chem.* 1999, 206, 107-132.
17. Subramaniam, B.; Busch, D.H. Use of Dense-Phase Carbon Dioxide in Catalysis. In *CO₂ Conversion and Utilization*. Song, C.; Eds.; Gaffney, A. M.; Fujimoto, K. American Chemical Society, Washington DC, 2001, in press.
18. Cooper, A. I. Polymer Synthesis and Processing Using Supercritical Carbon Dioxide. *J. Mater. Chem.* 2000, 10 (2), 207-234.
19. Xu, X.D.; Moulijn, J.A. Mitigation of CO₂ by Chemical Conversion: Plausible Chemical Reactions and Promising Products. *Energy & Fuels*, 1996, 10 (2), 305-325.
20. EIA/IEO. International Energy Outlook (IEO), Energy Information Administration, U.S. Department of Energy, DOE/EIA-0484(97), July 1998.
21. EIA/IEO. International Energy Outlook (IEO), Energy Information Administration, U.S. Department of Energy, 1999.
22. EIA/AER. Annual Energy Review (AER) 1997, Energy Information Administration, U.S. Department of Energy, Report No. DOE/EIA-0384(97), July 1998.
23. EIA/AER. Annual Energy Review (AER) 1998, Energy Information Administration, U.S. Department of Energy, 1999.
24. EIA/GHG. Emission of Greenhouse Gases in the United States 1999. Report No. EIA/DOE-0573(99), Energy Information Administration, US Department of Energy, October 31, 2000.
25. Lee, K.-W. Clean Fuels from Biomass. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46(1), 61-64.
26. EIA/AER. Annual Energy Review (AER) 1999, Energy Information Administration, US Department of Energy, September 2000.
27. DOE/EPA. Fuel Economy. Internet Resource Developed by U.S. Department of Energy and U.S. Environmental Protection Agency, <http://www.fueleconomy.gov/feg/atv.shtml>. Viewed May 20, 2001.
28. Manzer, L. E. CO₂ Emission Reductions: An Opportunity for New Catalytic Technology. In *CO₂ Conversion and Utilization*. Song, C.; Gaffney, A. M.; Fujimoto, K.; Eds.; American Chemical Society, Washington DC, 2001, in press.

29. DOE/OS-FE. Carbon Sequestration. State of the Science. Office of Science and Office of Fossil Energy, U.S. Department of Energy, February 1999.
30. Herzog, H.J.; Drake, E.M. Carbon Dioxide Recovery and Disposal from Large Energy Systems. *Ann. Rev. Energ. Env.*, 1996, 21, 145-166.
31. Herzog, H. J. Using Carbon Capture and Sequestration Technologies to Address Climate Change Concerns. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46(1), 53-55.
32. Chakma A. CO₂ Capture Processes - Opportunities for improved energy efficiencies. *Energy Conversion and Management*, 1997, 38, S51-S56.
33. Smith, I. M. CO₂ Reduction – Prospects for Coal. IEA Report No. CCC/26, IEA Coal Research, London, U.K., 1999, 84 pp.
34. Sander, M.T.; Mariz, C.L. The Fluor Daniel ECONAMINE FG Proces - Past Experience and Present-Day Focus. *Energy Conversion and Management*, 1992, 33 (5-8), 341-348.
35. Mariz C. L. Carbon Dioxide Recovery: Large Scale Design Trends. *J. Canadian Petroleum Technology*, 1998, 37 (7), 42-47.
36. Mimura, T.; Shimojyo, S.; Suda, T.; Iijima, M.; Mitsuoka, S. Development of Energy-Saving Absorbents for the Recovery of Carbon-Dioxide from Boiler Flue-Gas. *Kagaku Kogaku Ronbun*, 1995, 21 (3), 478-485.
37. Wolsky, A. M.; Daniels, E. J.; Jody, B. J. CO₂ Capture from the Flue-Gas of Conventional Fossil-Fuel-Fired Power-Plants. *Environ Prog.* 1994, 13 (3), 214-219.
38. Kikkinides, E. S.; Yang, R. T.; Cho, S. H. Concentration and Recovery of CO₂ from Flue-Gas by Pressure Swing Adsorption. *Ind. Eng. Chem. Res.*, 1993, 32 (11), 2714-2720.
39. Gottlicher G, Pruschek R. Comparison of CO₂ Removal Systems for Fossil-Fueled Power Plant Processes. *Energy Conversion and Management*, 1997, 38, S173-S178.
40. Meisen A.; Shuai, X.S. Research and Development Issues in CO₂ Capture. *Energy Conversion and Management*, 1997, 38, S37-S42.
41. Beecy, D. The Role of Carbon Sequestration in a National Carbon Management Strategy. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46 (1), 38-44.
42. Kane, R.; Klein, D. E. Opportunities for Advancements in Chemical Processes in Carbon Sequestration and Climate Change Mitigation. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46(1), 275-277.
43. Riemer, P. W. F.; Ormerod, W. G. International Perspectives and the Results of Carbon-Dioxide Capture, Disposal and Utilization Studies. *Energy Conversion and Management*, 1995, 36 (6-9), 813-818.
44. Koros, W.J.; Mahajan, R. Pushing the Limits on Possibilities for Large Scale Gas Separation: Which Strategies?. *J. Membrane Science*, 2000, 175 (2), 181-196.

45. (a) Song, C. Tri-reforming: A New Process for Reducing CO₂ Emissions. *Chemical Innovation* (formerly *Chemtech*, ACS), 2001, 31 (1), 21-26; (b) Song, C. Chemicals, Fuels and Electricity Co-generated from Coal. A Proposed Concept for Utilization of CO₂ from Power Plants. *Proceedings of 16th Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, October 11-15, 1999, Paper No. 16-5.
46. Ferguson, J. E. Carbon Dioxide. *MacMillan Encyclopedia of Chemistry*. MacMillan References, New York, Vo. 1, 1997, pp. 302-308.
47. Lange's HDBK. Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill, New York, 1985, p. 9-4 and p. 9-70.
48. CRC HDBK. CRC Handbook of Chemistry and Physics. 75th Edition, CRC Press, Boca Raton, FL, 1994, p.5-4.
49. Ormerod, W.; Riemer, P.; Smith, A. Carbon Dioxide Utilisation. IEA Greenhouse Gas R&D Programme, ISBN 1 898373 17 5, IEA, London, U.K., January 1995.
50. ACS. Facts & Figures for the Chemical Industry. *Chem. Eng. News*, June 26, 2000, 48-89.
51. ACS. Facts & Figures for the Chemical Industry. *Chem. Eng. News*, June 24, 1996, 38-79.
52. OTP (Office of technology Policy, U.S. Department of Commerce.). Meeting the Challenge: U.S. Industry Faces the 21st Century. *Chemtech*, 1996, 26, 46-54.
53. Audus H; Oonk H. An Assessment Procedure for Chemical Utilisation Schemes Intended to Reduce CO₂ Emissions to Atmosphere. *Energy Conversion and Management*, 1997, 38, S409-S414.
54. Armor, J. N. Catalytic Fixation of CO₂, CO₂ Purity, Energy, and the Environment. *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 2000, 45 (1), 141-142.
55. Choudhary, V.R.; Mamman, A. S.; Uphade, B. S.; Babcock, R. E. CO₂ Reforming and Simultaneous CO₂ and Steam Reforming of Methane to Syngas over Co_xNi_{1-x}O Supported on Macroporous Silica-Alumina Precoated with MgO. In *CO₂ Conversion and Utilization*. Song, C.; Gaffney, A. M.; Fujimoto, K.; Eds.; American Chemical Society, Washington DC, 2001, in press.
56. Aresta, M.; Quaranta, E. Carbon Dioxide: A Substitute for Phosgene. *Chemtech*, 1997, 27 (3), 32-40.
57. Aresta, M.; Dibenedetto, A.; Tommasi, I. Developing Innovative Synthetic Technologies of Industrial Relevance Based on Carbon Dioxide as Raw Material. *Energy & Fuels*, 2001, 15, 269-273.
58. Dibenedetto, A.; Aresta, M. Nb₂O₅ as Catalyst in the Oxidative Carboxylation of Olefins. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46(1), 119-121.

59. Markels, M.; Barber, R. T. Sequestration of Carbon Dioxide by Ocean Fertilization. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46(1), 45-48.
60. Steinberg, M. CO₂ Mitigation and Fuel Production. *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 2000, 45 (1), 74-76.
61. Steinberg, M. CO₂ Mitigation and Fuel Production. In *CO₂ Conversion and Utilization*. Song, C.; Gaffney, A. M.; Fujimoto, K.; Eds.; American Chemical Society, Washington DC, 2001, in press.
62. Beecy, D.; Ferrell, F. M.; Carey, J. K. Advanced Concepts for CO₂ Conversion, Storage, and Reuse. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 2001, 46 (1), 99-100.
63. Mahajan, D.; Song, C.; Scaroni, A. W. Micro-reactor Study on Catalytic Reduction of CO₂ into Liquid Fuels: Simulating Reactions under Geologic Formation Conditions. *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, 2000, 45 (1), 113-117.
64. Mahajan, D.; Song, C.; Scaroni, A. W. Catalytic Reduction of CO₂ into Liquid Fuels: Simulating Reactions under Geological Formation Conditions. . In *CO₂ Conversion and Utilization*. Song, C.; Gaffney, A. M.; Fujimoto, K.; Eds. American Chemical Society, Washington DC, 2001, in press.